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(54) Title: MAGNESIUM DIBORIDE SUPERCONDUCTORS

(57) Abstract: A method of manufacturing polycrystalline bulk MgB<sub>2</sub> with enhanced superconducting properties, by introducing structural defects forming pinning sites for quantised magnetic vortices, so as to prevent them from moving under the action of the Lorentz force.



**WO 03/049208 A2**

### "Magnesium Diboride Superconductors"

Magnesium Diboride ( $\text{MgB}_2$ ) was discovered to have superconducting properties  
5 in early 2001 [1]. The pure material is a type II superconductor with a superconducting  
transition temperature  $T_c$  of  $\sim 39\text{K}$ .

Magnesium Diboride falls between the classic low temperature superconductors  
(LTS) e.g. NbTi and NbSn with  $T_c$ 's under  $20^\circ\text{K}$ , and the newer High Temperature  
Superconductors (HTS) e.g. YBaCuO and BiSrCaCuO with  $T_c$ 's over  $90^\circ\text{K}$ .

10 LTS superconductors are most frequently operated at or near  $4^\circ\text{K}$  using liquid  
helium as a coolant. HTS superconductors have been targeted at an operating  
temperature as high as  $77^\circ\text{K}$  where liquid nitrogen could be used as the coolant.  
Magnesium Diboride shows promise for use at about  $20^\circ\text{K}$ , where relatively inexpensive  
closed cycle refrigerator cooling could be employed.

15 Unlike many of the HTS materials, supercurrent in the  $\text{MgB}_2$  system is not  
significantly hindered by grain boundaries. This means that long lengths of high  
performance polycrystalline materials may be easier to fabricate. In addition, the starting  
and sheathing materials of the  $\text{MgB}_2$  conductor are less expensive than those involved  
in the production of polycrystalline HTS conductors of the Bi based compounds, and  
20 much more simple than for the HTS conductors of the RE based compounds. The  
possibility of use at about  $20^\circ\text{K}$ , combined with the possible low cost in conductor  
fabrication would make  $\text{MgB}_2$  an attractive material for the Magnetic Resonance Imaging  
market (MRI) operated on  $20^\circ\text{K}$  cryocoolers, and other high current conductor  
applications.

25 Fragments of the pure material have been shown to support critical current  
density ( $J_c$ ) of over  $10^6 \text{ A/cm}^2$  at  $20^\circ\text{K}$  and zero applied field. However, in such  
fragments the critical current density falls to values below  $10^3 \text{ A/cm}^2$  at relatively low

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fields of between 3.5 and 4 T at 20°K [2]. This fall off in the  $J_c$  in bulk material with applied field appears to be more rapid than it is in the HTS materials at the same temperature.

The magnitude and field dependence of  $J_c$  are related to the presence of structural defects that can “pin” the quantised magnetic vortices that permeate the material and prevent them from moving under the action of the Lorentz force. Vortex studies suggest that it is the lack of suitable pinning sites in  $MgB_2$  that causes the rapid decay of  $J_c$  with field. [2]

If the vortex pinning could be strengthened so as to increase  $J_c$  in magnetic fields of a few Tesla then  $MgB_2$  could compete both on price and performance with the HTS alternatives when operated at about 20°K.

It has been shown that low levels of atomic disorder, introduced by proton irradiation enhance the pinning and so increase  $J_c$  significantly at high fields. [3]

Irradiation is not a viable technique for large scale conductor fabrication. Accordingly, the present application provides a method of enhancing the superconducting properties of polycrystalline bulk  $MgB_2$  by modifying the process of manufacturing the material in such a way as to give rise to structural defects forming pinning sites for quantised magnetic vortices, so as to prevent them from moving under the action of the Lorentz force.

A first preferred method according to the present invention comprises the step of introducing specific chemical impurities, chosen on the basis of their ionic radius and ionic charge. Suitable materials include Si, Cu, Zn and Al, C, Li, and N

A second preferred method according to the present invention comprises the step of introducing particles of a material chosen for its nano-particle starting size. The additive should be a material which remains in the same form after reaction, or

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something that reacts to form a nano-boride phase. A preferred material for this purpose is  $Y_2O_3$  [4]

In the first preferred method, the additive is preferably introduced in nominal concentrations between 1% and 5% atomic percent during a solid state reaction between Mg, B and the additive. Preferably the concentration is about 3 at.%. In the second preferred method, the additive is preferably introduced in concentration of 5-15 wt. %. Preferably the concentration is about 10 wt. %.

Preferably B, Mg and alloying additive are mixed, pressed into pellets and then sintered in an inert atmosphere (5%  $H_2$  in Ar or in N/Ar ) in a reaction which involves a 15-minute anneal at 900°C. Excess Mg is present in the reaction chamber to ensure the formation of  $MgB_2$ .

A third preferred method according to the invention is characterised by the time of reaction and the precise form of the B starting precursor.  $MgB_2$  made using commercially obtained amorphous B powder appears to yield a shallow dependence of  $J_c$  on field, similar to the effect of the alloying additions and  $Y_2O_3$  nano-particle additions. A short reaction time is also beneficial, with 15 minutes at 900°C better than longer reaction times (e.g. 60 minutes).

Figure 1 shows the form of the precipitates which result when 10 wt. %  $Y_2O_3$  is reacted with the Mg+B. A nano-phase of  $YB_4$  results in a very fine and even distribution.

The graph of Figure 2 shows the critical current  $J_c$  normalised by  $J_c$  at 2T field 20°K of the  $MgB_2$  + various dopants measured using a magnetisation method. Also shown is the  $J_c$  behaviour for an undoped  $MgB_2$  made by a standard reaction route as well as  $MgB_2$  made by a rapid reaction route (15 min. 900°C) using an amorphous B precursor powder.

The graph shows the following different samples:

$MgB_2$  + 3 at. % Zn,  $MgB_2$  + 3 at.% Cu,  $MgB_2$  + 3 at.% Al,  $MgB_2$

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MgB<sub>2</sub> + 10wt % Y<sub>2</sub>O<sub>3</sub> nanoparticles

MgB<sub>2</sub> undoped sample made by a standard route (60min anneal at 900°C)

MgB<sub>2</sub> undoped sample made by a 'special' route (15min anneal at 900°C)

Because the pellets are not fully dense and unlikely to be fully connected it is not  
5 possible to directly compare the exact values of J<sub>c</sub> as obtained by the method of  
measurement. Hence the normalised method is more informative. What is of  
importance is the rate at which the J<sub>c</sub> is being diminished with increasing field i.e. the  
gradient of the J<sub>c</sub>(B) plot.

The addition of the dopants, and in particular the Al and the Y<sub>2</sub>O<sub>3</sub>, as well as rapid  
10 reaction of undoped material to induce disorder, prolongs to much higher fields the  
value at which J<sub>c</sub> drops below 1000 A/cm<sup>2</sup>. This suggests that the pinning has been  
strengthened considerably by the addition of the dopants.

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## CLAIMS

1. A method of manufacturing polycrystalline bulk  $\text{MgB}_2$  with enhanced superconducting properties, by introducing structural defects forming pinning sites for quantised magnetic vortices, so as to prevent them from moving under the action of the Lorentz force.
2. A method according to claim 1 in which the structural defects are formed by including a specific chemical impurity chosen for its ionic radius and ionic charge.
3. A method according to claim 2 in which the impurity comprises one or more of Si, Cu, Zn, Al, C, Li, or N.
4. A method according to claim 3 in which the invention is introduced in a nominal concentration of between 1 and 5 at.% during a solid state reaction between Mg, B and the additive.
5. A method according to claim 1 in which the structural defects are formed by including an additive chosen on the basis of its inert nature or ability to react with B to form a nano-boride phase of nano particle starting size.
6. A method according to claim 5 in which the additive is introduced in a concentration of 5-15 wt.% during a solid state reaction between Mg, B and the additive.
7. A method according to claim 5 or claim 6 in which the additive comprises  $\text{Y}_2\text{O}_3$ .
8. A method according to claim 4 in which the concentration is 3 at.%.
9. A method according to claim 6 in which the concentration is 10 wt.%.

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10. A method according to claim 1 in which structural defects are formed by utilising commercially grade amorphous B powder and annealing for a relatively short time to produce an inherently disordered structure.
11. A method according to any one of the preceding claims in which the materials  
5 are mixed, pressed into pellets and then sintered in an inert atmosphere in a reaction which includes annealing in an Mg –rich environment.
12. A method according to claim 10 or claim 11 in which the annealing is performed for 15 minutes at 900°C.
13. A superconducting material comprising bulk polycrystalline  $\text{MgB}_2$  made by the  
10 method of any one of the preceding claims.

Figure 1





